Abstract

The present thesis deals with the synthesis of ligand system containing nitrogen, phenolate as well as carboxylate donor sites. Stable copper coordinated phenolate radical has been synthesized which are structural models of the enzyme galactose oxidase. Macrocyclic ligand containing amide donor sites has been designed and its coordination behaviour towards copper studied.

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. The importance of the chemistry of copper in general and biochemistry of copper in particular is highlighted. The structure and function of the various copper containing enzymes are also described in this chapter. In addition this chapter projects the scope of work on the chosen aspects of copper chemistry and a brief survey of the work done so far.

Chapter 2 describes the details of the methods of elemental analyses and instruments/equipment used for characterization and structural assessment of the newly synthesized compounds and also for studies of various reactions.

Structural models to study the Cu–N interactions of a number of enzymes, notably those involved in the catalysis of electron transfer, in transport of dioxygen and the catalysis of its reactions forms the basis of **chapter 3**. New ligands containing 3,5–dimethyl pyrazole has been synthesized and characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy. The copper(II) complex of the ligand containing P=O group was prone to P–N bond hydrolysis due to the presence of chlorine attached to phosphorus atom.

Chapter 4 deals with the structural model of galactose oxidase. The highlights of the content of this chapter are the synthesis of two new pentadentate ligands, N,N'–bis(2–hydroxybenzyl) ethylenediamine N–acetic acid [$L^{1}H_3$] and N,N'–bis[(2–hydroxy, 3,4–di–*tert*–butyl)benzyl]ethylenediamine N–acetic acid [$L^{2}H_3$] and the synthesis of N,N',N', tris(2–hydroxybenzyl) ethylenediamine [$L^{3}H_3$] by a modified method and their corresponding copper(II) complexes, K[CuL].H_2O.

The ligands have been characterized by elemental analyses, IR, ^{1}H and ^{13}C

NMR spectroscopy. The complexes have been characterized by elemental analyses, IR, UV–visible, TGA, DTA, cyclic voltammetry, conductivity measurements and EPR spectroscopy. The spectral studies suggest that the ligand acts in a pentadentate fashion and the complexes have a square pyramidal elongated structure. Cyclic voltammogram of $K[CuL^2].H_2O$ showed two quasi reversible peaks due to phenolate radical generation. The presence of a radical species has also been proved. The complexes are therefore structural models of the enzyme galactose oxidase.

Chapter 5 deals with the synthesis and characterization of a heteroleptic tripodal ligand, bis(2–hydroxy, 3,5–ditertiary butyl benzyl) N–acetic acid, BHDBBA, and its copper(II) complex. The ligand has been prepared from 2,4–ditertiary butyl phenol, paraformaldehyde and glycine by Mannich reaction. Characterization has been done by elemental analyses, IR, ^1H and ^{13}C NMR spectroscopy. The copper complex has also been characterized by elemental analyses, IR, UV–visible, cyclic voltammetry, conductivity measurements and EPR spectroscopy. The spectroscopic measurements clearly indicate the generation of a radical species on oxidation of the complex with ammonium cerium(IV) nitrate. The EPR spectrum of the complex indicates a $d_{x^2-y^2}$ ground state with a minor rhombic perturbation perhaps indicative of a distortion towards a trigonal bipyramidal structure. The complex also represents an active site model for galactose oxidase.

Chapter 6 indeed the concluding chapter of the thesis, deals with the synthesis of a polyamide macrocyclic ligand (LH_6), prepared from triethyl ester of nitrilotriacetic acid and 1,2–diamino benzene, and its characterization by elemental analyses, IR, ^1H and ^{13}C NMR spectroscopy. Copper complex of the ligand, $[Cu(LH_6)Cl_2]$ have been synthesized and characterized by elemental analyses, IR, UV–visible, conductivity measurements, cyclic voltammetry and EPR spectroscopy.